

# Exciton scattering in light-harvesting systems of purple bacteria

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Using the reduced density matrix formalism the exciton scattering in light-harvesting systems of purple bacteria is calculated. The static disorder (fluctuations of the site energies) as well as the dynamic disorder (dissipation) is taken into account in this work. Circular aggregates with 18 pigments are studied to model the B850 ring of bacteriochlorophylls with LH2 complexes. It can be shown that the influence of dissipation may not be neglected in the simulation of the time-dependent anisotropy of fluorescence. Also an elliptical deformation of the ring could be essential.

*Key words:* exciton transfer, density matrix theory, fluorescence

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## 1 Motivation

Highly efficient light collection and excitation transfer to the reaction center initiates the energy conversion in photosynthesis. This process takes place in the so-called light-harvesting antenna network. Particularly, the ring subunit of the peripheral light-harvesting antenna (LH2) [1] of purple bacteria has been extensively studied [2]. The very symmetric arrangement with short distances between the pigments gave new impulses to the discussion about coherence in the exciton transfer and the exciton delocalization in LH2. Both could be reduced by dynamic and static disorders.

Time-dependent experiments made it possible to study the femtosecond dynamics of the energy transfer and relaxation [3]. Kumble and Hochstrasser [4] have presented a time-domain analysis of the effects of the static disorder upon the dynamics of optical excitations. The interpretation of time-dependent experiments on the femtosecond time scale requires a theory which incorporates static and dynamic disorder. The aim of the present paper is to extend the investigation by Kumble and Hochstrasser taking into account the simultaneous influence of static and dynamic disorders after impulse excitation. In addition we calculate the time-dependent anisotropy of fluorescence not only for the symmetric but also for elliptically distorted rings.

## 2 Model

The Hamiltonian

$$H = H_{\text{ex}}^0 + H_{\text{ph}} + H_{\text{ex-ph}} + H_{\text{s}} + H_{\text{el}} \quad (1)$$

describes the transfer of a single exciton with a transfer integral  $J$  along the ideal ring ( $H_{\text{ex}}^0$ ), the independent heat baths for each chromophore ( $H_{\text{ph}}$ ), the

site-diagonal and linear interaction between the exciton and the bath ( $H_{\text{ex-ph}}$ ), the static disorder ( $H_s$ ) with Gaussian distribution (standard deviation  $\Delta$ ) and elliptical distortion of the ideal ring ( $H_{\text{el}}$ ).

Diagonalization of the Hamiltonian  $H_{\text{ex}}^0$  of the ideal ring leads to eigenstates  $|k\rangle$  and eigenenergies  $E_k = -2J \cos k$ . For a symmetrical coplanar arrangement of site transition moments  $\vec{\mu}_n$  dipole-allowed transitions populate only the degenerate  $k = \pm 1$  levels of the ideal ring. If the ring is elliptically distorted the eigenenergies of the Hamiltonian  $H_{\text{ex}}^0 + H_{\text{el}}$  are no longer degenerate as is the case for the ideal ring. With static disorder of the site energies being present ( $\Delta \neq 0$ ), the stationary states, i.e. the eigenstates  $|a\rangle$  of the Hamiltonian  $H_{\text{ex}}^0 + H_s$ , correspond to mixtures of  $|k\rangle$  and an excitation will prepare a superposition of the  $|k\rangle$  states.

The dipole strength  $\vec{\mu}_a$  of state  $|a\rangle$  of the ring with static disorder and the dipole strength  $\vec{\mu}_\alpha$  of state  $|\alpha\rangle$  of the ideal one read

$$\vec{\mu}_a = \sum_{n=1}^N c_n^a \vec{\mu}_n, \quad \vec{\mu}_\alpha = \sum_{n=1}^N c_n^\alpha \vec{\mu}_n. \quad (2)$$

The coefficients  $c_n^\alpha$  and  $c_n^l$  are the expansion coefficients of the eigenstates of the ideal and disordered rings in site representation.

Kumble and Hochstrasser [4] concluded, that in the case of pump pulse excitation the dipole strength is simply redistributed among the exciton levels due to disorder. So the amplitudes of site excitations and the phase relationships in the initial state are necessarily identical to that of an equal superposition of  $k = \pm 1$  excitons of the ideal ring. Thus, generally, the excitation with a pump pulse of sufficiently wide spectral bandwidth will always prepare the same initial state, irrespective of the actual eigenstates of the real ring. The nature of this initial state is entirely determined by the selection rules of the ring without static disorder. The initial condition for the density matrix by

pulse excitation with the polarization  $\vec{e}_x$  is given by (Eq. (1a) in [5]):

$$\rho_{\alpha\beta}(t=0; \vec{e}_i) = \frac{1}{A}(\vec{e}_x \cdot \vec{\mu}_\alpha)(\vec{e}_x \cdot \vec{\mu}_\beta), \quad (3)$$

where  $A = \sum_\alpha (\vec{e}_x \cdot \vec{\mu}_\alpha)(\vec{e}_x \cdot \vec{\mu}_\alpha)$ .

### 3 Anisotropy of fluorescence

Kumble and Hochstrasser [4] calculated the usual time-dependent anisotropy of fluorescence

$$r(t) = \frac{\langle S_{xx}(t) \rangle - \langle S_{xy}(t) \rangle}{\langle S_{xx}(t) \rangle + 2\langle S_{xy}(t) \rangle} \quad (4)$$

where, e.g.,

$$\langle S_{xy}(t) \rangle = \langle |\sum_{\alpha, l, n} (\vec{e}_x \cdot \vec{\mu}_\alpha)(\vec{e}_y \cdot \vec{\mu}_l) c_n^{\alpha*} c_n^l e^{-i\omega_l t}|^2 \rangle. \quad (5)$$

The indices  $\alpha$  and  $l$  label the eigenstates of the virtual and disordered ring, respectively. The brackets  $\langle \rangle$  denote the ensemble average and the average over the direction of the laser pulses with fixed relative directions  $\vec{e}_x$  and  $\vec{e}_y$ .

To include the dynamic disorder which contributes to dephasing of the initial wave packet and promotes thermalization of the dephased populations one has to work within the exciton density matrix formalism [6] instead of using only the exciton wave functions

$$S_{xy}(t) = \int P_{xy}(\omega, t) d\omega \quad (6)$$

where

$$P_{xy}(\omega, t) = A \sum_l \sum_{l'} \rho_{ll'}(t) (\vec{e}_y \cdot \vec{\mu}_{l'}) (\vec{e}_y \cdot \vec{\mu}_l) [\delta(\omega - \omega_{l'0}) + \delta(\omega - \omega_{l0})]. \quad (7)$$

## 4 Density matrix formalism for exciton transfer and relaxation

Provided that the exciton dynamics is not very fast, its coupling to the bath weak, and except for the initial time-interval  $t \lesssim t_d$  ( $t_d$  = dephasing time of the bath), the adequate equation for a factorized initial state is the Redfield equation [7,8]:

$$i\frac{d}{dt}\rho(t) = \frac{1}{\hbar}[H, \rho(t)] + \mathcal{R}\rho(t), \quad (8)$$

The Redfield relaxation superoperator  $\mathcal{R}$  describes the influence of the thermal bath on the dynamics of the exciton.

Čápek applied several different ways of obtaining of convolutional and convolutionless dynamical equations for the exciton density matrix in the site basis [9]. After Markovian approximation they have the following form

$$i\frac{d}{dt}\rho(t) = \frac{1}{\hbar}[H, \rho(t)] - \delta\Omega\rho(t). \quad (9)$$

We proved [6] the equivalence of the Redfield theory without secular approximation with Čápek's equations after Markovian approximation.

## 5 Results

In Kumble and Hochstrasser's modeling, the anisotropy of fluorescence of the ring LH2 subunit decreases from 0.7 to 0.3–0.35 and subsequently establishes a final value of 0.4. Kumble and Hochstrasser concluded that one needs static disorder of strength  $\Delta \approx 0.4 - 0.8J$  to reach a time decay below 100 fs .

Our results for the time dependence ( $t = \tau\hbar/J$ ) of the anisotropy of fluorescence Eq. (4) in the symmetrical ring are shown on Fig. 1 with static disorder  $\Delta/J = 0.4$ . In addition we consider two strengths of dynamic disorder

$j_0 = 0.2, 0.4$  entering the spectral density  $J(\omega) = \Theta(\omega)j_0\frac{\omega^2}{2\omega_c^3}e^{-\omega/\omega_c}$  with cut-off frequency  $\omega_c = 0.2J$  [10]. Inclusion of dynamic disorder leads to faster decay of the anisotropy of fluorescence during the initial stage. Smaller strength of the static disorder  $\Delta/J$  than predicted by Kumble and Hochstrasser would be necessary to guarantee the decrease of the anisotropy of fluorescence during the first 100 fs.

It was concluded in Ref. [4] based on measurements by Chachisvilis et al. [11] that the time decay of the anisotropy of fluorescence during the first dozens of fs is *temperature independent* in the case of LH2 subunits. Our calculation for the symmetrical ring show that such result can be obtained only for  $\Delta > 0.8$ . But because the time resolution of the experiments in [11] was not too high this very restrictive statement about the strength of the static disorder can only be made with caution. We expect that some temperature dependence can be seen using experiments with shorter laser pulses.

Recent results obtained by single molecule spectroscopy [12] can only be interpreted [13] admitting the presence of a  $C_2$  distortion of the LH2 ring. It has, up to now, not been concluded whether such  $C_2$  distortion of the LH2 ring is present also in samples in vivo.

We have made calculations which take into account the possible  $C_2$  distortion of the ring using the model C by Matsushita et al. [13] of elliptical distortion of the ring in which the transfer integral  $J$  is cosine modulated. Local transition dipole moments lie tangentially to the ellipse. Our results for the time dependence of the anisotropy of fluorescence (4) in the elliptically distorted ring are shown on Fig. 2 with the static disorder  $\Delta/J = 0.4$  and the strength of the dynamic disorder  $j_0 = 0.2$  for three values of the elliptical deformation  $V_2/J = 0.05, 0.1, 0.2$ .

It is seen, that the inclusion of an elliptical deformation leads to faster decay of the anisotropy of fluorescence and diminishes the influence of the dynamic dis-

order. Our calculation for the elliptically distorted ring ( $V_2/J = 0.2$  [13]) show that the *temperature independent* time decay of the anisotropy of fluorescence during the first dozens of fs can be obtained even for  $\Delta \approx 0.4$ .

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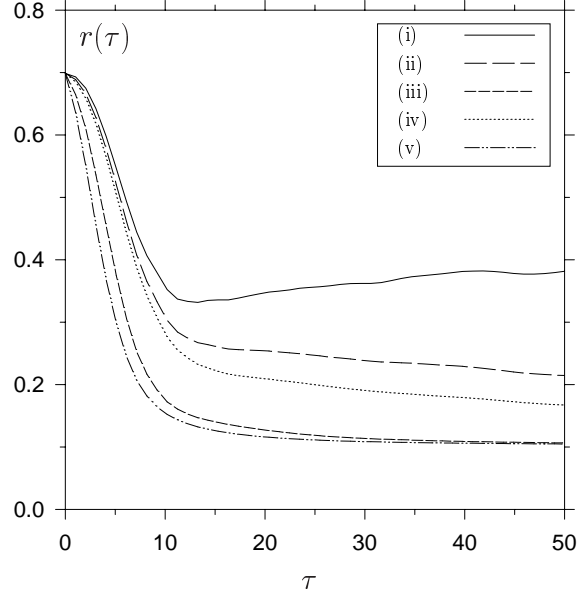


Fig. 1. Time dependence of the anisotropy of fluorescence  $r(\tau)$  for the symmetrical ring with the static disorder  $\Delta/J = 0.4$ . The influence of the dynamic disorder is displayed by curves for low (ii), (iv) and room temperature (iii), (v) for  $j_0 = 0.2$  (ii), (iii), and  $j_0 = 0.4$  (iv), (v) compared to  $j_0 = 0.0$  (i).

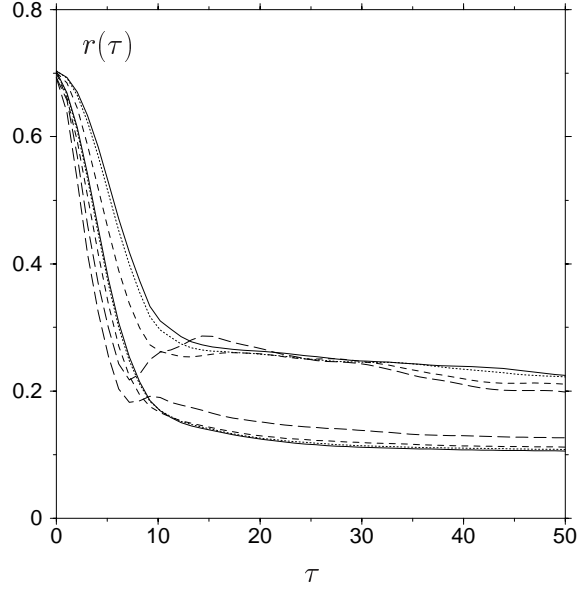


Fig. 2. Time dependence of the anisotropy of fluorescence  $r(\tau)$  for the elliptically distorted ring with the static disorder  $\Delta/J = 0.4$  and dynamic disorder  $j_0 = 0.2$ . The influence of the elliptical deformation displayed by dotted lines for  $V_2/J = 0.05$ , dashed lines for  $V_2/J = 0.1$  and long dashed lines for  $V_2/J = 0.2$  compared to  $V_2/J = 0.0$  (solid lines) for low and room temperature.